

VERIFICATION OF TRANSLATION

Re : Japanese Patent Application No. 2000-147239

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Dated this 9th day of January, 2004



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PATENT OFFICE
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[List of Annexed Documents]

[Document]	Specification	1
[Document]	Abstract	1
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[Document] Specification

[Title of the Invention] Process for Preparing Polyurethane Foam

[Claims]

[Claim 1] A process for preparing a polyurethane foam, comprising reacting a polyol component having a number-average molecular weight of 1000 to 2400 with a polyisocyanate compound in the presence of a catalyst and a blowing agent, to give a molded article having a density of 0.4 to 0.8 g/cm³, and heat-treating the resulting molded article to a temperature of not less than 60°C.

[Claim 2] The process according to claim 1, wherein the molding is carried out to give a molded article having a hardness of 50 to 75 (Asker C).

[Claim 3] The process according to claim 1 or 2, wherein the ratio of the polyol component to the polyisocyanate compound is adjusted so that an isocyanate index is 90 to 110.

[Claim 4] The process according to any one of claims 1 to 3, wherein the polyol component is a polyester-polyol.

[Claim 5] The process according to any one of claims 1 to 4, wherein the compression set is 15 to 25%.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a process for preparing a polyurethane foam. More specifically, the present invention relates to a process for preparing a polyurethane foam which can be suitably used for cushioning materials such as shoe soles, and the like.

[0002]

[Prior Art]

When a polyurethane foam is used as a cushioning material for shoe soles of sports shoes, its compression set (as prescribed in ASTM D 395, hereinafter referred to the same) is important. Therefore, it has been desired to satisfy both compression set and strength. However, it is actually difficult to meet both properties. For instance, if the crosslinking density of a polyurethane foam is increased in order to improve the strength, the compression set is, on the other hand, lowered.

[0003]

Japanese Patent Laid-Open No. Hei 7-179556 discloses a process for preparing a polyurethane having a high hardness (not less than 75 as prescribed in JIS-A), and being excellent in heat resistance, compression permanent strain and cold resistance, comprising reacting a polyester-polyol having a molecular weight of 2500 to 3500 and 1,4-butanediol with a diisocyanate in a specific ratio. However, there are some defects in this process that the polyurethane foam is poor in heat resistance, compression permanent strain and cold resistance, in a desired molded article density range (0.4 to 0.8 g/cm^3) at Asker C hardness of 50 to 75.

[0004]

Japanese Patent Laid-Open No. Hei 7-179557 discloses a process for preparing a thermoplastic polyurethane which is excellent in moldability and has good heat resistance and cold resistance, comprising 1,9-nonanediol and 3-methyl-1,5-pentanediol as essential components for specific polyester diols. However, this polyurethane has some defects in that the polyurethane foam is poor in heat resistance, compression permanent strain and cold resistance, in a

desired molded article density range (0.4 to 0.8 g/cm³) at Asker C hardness of 50 to 75.

[0005]

Also, Japanese Patent Laid-Open No. Hei 7-271263 discloses a process for preparing a cleaning blade comprising a thermoplastic polyurethane elastomer. This process is characterized in that heat treatment is carried out at a temperature of 60° to 100°C for 8 to 16 hours to give a hardness (JIS-A) of 50 to 80, whereby a cleaning blade having a compression set (compression permanent strain) of not more than 30% is obtained. However, this cleaning blade has some defects in that the cleaning blade is poor in heat resistance, compression permanent strain and cold resistance, in a desired molded article density range (0.4 to 0.8 g/cm³) at Asker C hardness of 50 to 75.

[0006]

[Problems to Be Solved by the Invention]

An object of the present invention is to provide a process for preparing a polyurethane foam retaining high strength within a specific molded article density range and being excellent in compression set, which can be suitably used as cushioning materials such as shoe soles of sports shoes, and the like.

[0007]

[Means to Solve the Problems]

Specifically, the present invention relates to a process for preparing a polyurethane foam, comprising reacting a polyol component having a number-average molecular weight of 1000 to 2400 with a polyisocyanate compound in the presence of a catalyst and a blowing agent, to give a molded article having a density of 0.4 to 0.8 g/cm³, and heat-treating the resulting molded article to a

temperature of not less than 60°C.

[0008]

[Modes for Carrying out the Invention]

The polyol component includes polyester-polyols, polyether-polyols and the like. Among them, the polyester-polyols are preferable from the viewpoint of satisfying both strength and compression set.

[0009]

The dicarboxylic acid constituting the polyester-polyol includes, for instance, saturated aliphatic dicarboxylic acids such as glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid; saturated alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid; aromatic dicarboxylic acids such as phthalic acid, terephthalic acid and isophthalic acid; unsaturated aliphatic dicarboxylic acids such as maleic acid, fumaric acid and itaconic acid; halogen-containing dicarboxylic acids such as tetrabromophthalic acid; ester-formable derivatives thereof; acid anhydrides thereof; and the like. These can be used alone or in admixture of two or more kinds. The dicarboxylic acid may contain a polybasic acid having not less than three functional groups, such as trimellitic acid or pyromellitic acid.

[0010]

The diol constituting the polyester-polyol includes, for instance, ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, methylpentanediol, 1,6-hexanediol, trimethylolpropane, glycerol, pentaerythritol, diglycerol, dextrose, sorbitol, and the like. These can be used alone or in admixture of two or more kinds.

[0011]

Representative examples of the polyether-polyol are polyoxypropylene-polyol (hereinafter referred to as "PPG"), polyoxytetramethylene glycol (hereinafter referred to as "PTMG"), and mixtures thereof.

[0012]

The PPG can be prepared by a process comprising subjecting a compound having at least two active hydrogens as a starting material to a usual ring-opening addition reaction of an alkylene oxide, and further adding ethylene oxide in a block form to the molecular terminal of the resulting compound, and the like.

[0013]

The compound having at least two active hydrogens includes, for instance, polyhydric alcohols, polyhydric phenols, polyamines, alkanolamines, and the like. Concrete examples of the compound having at least two active hydrogens include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, diglycerol, dextrose, sucrose, bisphenol A, ethylenediamine, and modified products thereof, and the like. These can be used alone or in admixture thereof.

[0014]

The alkylene oxide includes, for instance, ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, styrene oxide, and the like.

[0015]

The polyisocyanate compound includes aromatic, alicyclic and aliphatic polyisocyanates having at least two isocyanate groups, mixtures thereof, and modified polyisocyanates obtained by modifying those polyisocyanate

compounds. Concrete examples of the polyisocyanate compound include aromatic polyisocyanates such as tolylene diisocyanate, methylenediphenyl diisocyanate, naphthylene diisocyanate, xylylene diisocyanate and polymethylenepolyphenylene diisocyanate; alicyclic polyisocyanates such as hydrogenated methylenediphenyl diisocyanate, hydrogenated tolylene diisocyanate and isophorone diisocyanate; aliphatic polyisocyanates such as hexamethylene diisocyanate and lysine diisocyanate; mixtures thereof; modified products thereof; and the like. The modified products include, for instance, prepolymer-modified products which are reaction products of the polyisocyanate with the polyol, nurate-modified products, urea-modified products, carbodiimide-modified products, arophanate-modified products, burette-modified products, and the like.

[0016]

The catalyst includes, for instance, tertiary amines such as TEDA [1,4-diazabicyclo(2.2.2)octane], N,N,N',N'-tetramethylhexamethylenediamine, N,N,N',N'-tetramethylpropylenediamine, N,N,N',N',N''-pentamethyldiethylenetriamine, trimethylaminoethylpiperazine, N,N-dimethylcyclohexylamine, N,N-dimethylbenzylamine, N-methylmorpholine, N-ethylmorpholine, triethylamine, tributylamine, bis(dimethylaminoalkyl)piperazines, N,N,N',N'-tetramethylethylenediamine, N,N-diethylbenzylamine, bis(N,N-diethylaminoethyl) adipate, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethyl- β -phenylethylamine, 1,2-dimethylimidazole and 2-methylimidazole; organometal compounds such as dibutyltin dilaurate,

stannous oleate, cobalt naphthenate and lead naphthenate; and the like. These can be used alone or in admixture of two or more kinds.

[0017]

It is desired that the amount of the catalyst used is not less than 0.3 parts [parts by weight, hereinafter referred to the same], preferably not less than 0.5 parts, from the viewpoint of demoldability, and not more than 2.0 parts, preferably not more than 1.6 parts, from the viewpoints of filling ability and moldability, based on 100 parts of the polyol component.

[0018]

The blowing agent includes water, low-boiling point hydrocarbon compounds, chlorofluorocarbons, hydrogenated fluorocarbons, and the like. These can be used alone, or in admixture of two or more kinds. Among them, water is preferable. It is desired that the amount of the blowing agent used is 0.1 to 1.5 parts, preferably 0.2 to 1.0 part, based on 100 parts of the polyol component, from the viewpoint of lowering the density of a molded article, and from the viewpoints of reaction balance between resinifying and blowing, and moldability.

[0019]

In the present invention, auxiliaries such as surfactants, crosslinking agents, pigments, antioxidants and yellowing preventives can be employed in proper amounts as occasion demands.

[0020]

The surfactants include, for example, silicone surfactants such as polyalkylsiloxane, polyoxyalkylene polyol-modified dimethylpolysiloxane and alkylene glycol-modified dimethylpolysiloxane; and anionic surfactants such as

salts of fatty acids, salts of sulfuric acid esters, salts of phosphoric acid esters and sulfonates.

[0021]

The crosslinking agent includes low-molecular compounds having at least two groups selected from the group consisting of hydroxyl group, primary amino group, secondary amino group, and other active hydrogen-containing groups which are reactive with an isocyanate group.

[0022]

Concrete examples of the crosslinking agent include polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, glycerol, trimethylolpropane, triethanolamine and alkylene oxide adducts of bisphenol A; polyamines such as diethyltoluenediamine, chlorodiaminobenzene, ethylenediamine and 1,6-hexanediamine; and the like, without intending to limit the present invention to those exemplified ones. These crosslinking agents can be used alone or in admixture of two or more kinds. Among them, 1,4-butanediol and ethylene glycol are preferable.

[0023]

As a process for preparing a polyurethane foam, there can be cited, for instance, a process comprising previously mixing a polyol component, a catalyst, a blowing agent, an auxiliary, and the like with stirring to give a polyol solution; mixing the polyol solution with a polyisocyanate compound with stirring in a molding machine; and injecting the resulting mixture into a mold to foam. More specifically, there can be cited a process which comprises mixing a polyol component with stirring using a tank or the like, controlling the temperature of

the polyol component usually to 35° to 45°C, and reacting the polyol component with the polyisocyanate compound using a foaming machine such as an automatically mixing and injecting foaming machine or an automatically blending and injecting foaming machine to foam, and the like.

[0024]

It is desired that the ratio of the polyol component to the polyisocyanate compound is adjusted so that an isocyanate index is 90 to 110, more preferably 95 to 105, especially preferably 99 to 101, from the viewpoints of improvements in strength and flexural resistance.

[0025]

The molded article density of the molded article obtained by molding is controlled to 0.4 to 0.8 g/cm³, preferably 0.5 to 0.7 g/cm³, from the viewpoints of maintaining the strength and improving compression set of a polyurethane foam, in consideration of its use as a cushioning material for shoe soles. This molded article density can be controlled by regulating the amounts of the blowing agent and the catalyst.

[0026]

When the molded article is used as a cushioning material for shoe soles, it is preferable that the hardness of the molded article is controlled to 50 to 75 (Asker C), preferably 55 to 70 (Asker C), from the viewpoints of maintaining the strength and improving compression set of a polyurethane foam. The hardness of the molded article can be controlled by adjusting the amount of the crosslinking agent.

[0027]

Next, the resulting molded article is heat-treated at a temperature of not

less than 60°C. One of the great features of the present invention resides in that the molded article is heat-treated as described above. By heat-treating the molded article, there are exhibited some excellent effects that tensile strength and tear strength of the molded articles are improved, and moreover the compression set is also improved.

[0028]

The temperature of the heat treatment is not less than 60°C, preferably 80° to 100°C, more preferably 95° to 100°C, from the viewpoint of avoiding the molded article from being thermal deformed.

[0029]

The heat treatment serves to effectively accelerate the polyaddition reaction and the polymerization of the polyurethane foam. However, excessive heat treatment causes discoloration (yellowing) and thermal deformation of a polyurethane foam. Therefore, in consideration of suppression of the generation of these two phenomena and improvement in operability (productivity), it is preferable that heat treatment is carried out within a time period and at a temperature which accelerate the polymerization without discoloring or thermally deforming a polyurethane foam.

[0030]

The polyurethane foam obtained according to the process of the present invention has an excellent compression set of 10 to 25%, preferably 15 to 25%, so that the polyurethane foam has a sufficient strength. Therefore, the polyurethane foam can be suitably used as cushioning materials for shoe soles of sports shoes and the like.

[0031]

[Examples]

Examples 1 to 8 and Comparative Examples 1 to 8

The components used in each of Examples and Comparative Examples are as follows:

[0032]

[Polyol Component]

- Polyol A: A mixture prepared by mixing 40 parts of a polyester-polyol (polyethylene-1,4-butanediol adipate; number-average molecular weight: 2200) with 60 parts of a polyester-polyol (polyethylene-1,4-butanediol adipate; number-average molecular weight: 1300), with heating to a temperature of 60°C [acid value: 0.21 KOH mg/g, hydroxyl value: 72.3 KOH mg/g, water content: 0.82% by weight]
- Polyol B: Polyether-polyol [number-average molecular weight 2000; commercially available from HODOGAYA CHEMICAL CO., LTD. under the trade name of PTG-200SNW]

[0033]

[Polyisocyanate Compound]

- Polyisocyanate Compound A: commercially available from Kao Corporation under the trade name of EDDYFOAM B-2009
- Polyisocyanate Compound B: commercially available from Kao Corporation under the trade name of EDDYFOAM B-6106M

[0034]

[Catalyst]

- TEDA [1,4-diazabicyclo(2.2.2)octane]

[0035]

[Blowing Agent]

- Water

[0036]

[Crosslinking Agent]

- 1,4-Butanediol (hereinafter referred to as BD)
- Ethylene glycol (hereinafter referred to as EG)

[0037]

[Surfactant]

- Polyalkylsiloxane [commercially available from Nippon Unicar Company Limited under the trade name of SZ-1642] (hereinafter referred to as SZ-1642)

[0038]

The polyol component, the catalyst, water, the crosslinking agent and the surfactant were weighed in given amounts as shown in Tables 1 and 2, and the components were mixed with stirring, to give a polyol solution.

[0039]

The isocyanate index showing the mixing ratio of the polyol solution to the polyisocyanate compound was determined in accordance with the following equation:

[Isocyanate Index]

$$= 100 \times \left[\frac{\text{Amount of isocyanate actually used (parts)}}{\text{amount of isocyanate stoichiometrically equivalent to the amount of the polyol (parts)}} \right]$$

[0040]

Next, one of the tanks of pouring-type low-pressure blowing machine was charged with the polyol solution in an amount shown in Table 1, and the liquid

temperature was adjusted to 35° to 45°C. The other tank was charged with the polyisocyanate compound, and the liquid temperature was adjusted to 35° to 40°C.

[0041]

The polyol solution and the polyisocyanate compound were mixed with stirring by using the above-mentioned blowing machine, and the mixture was injected into a mold, and allowed to foam, to give a polyurethane foam of 100 mm × 300 mm × 10 mm.

[0042]

Next, the polyurethane foam obtained in each example was heated to a temperature of 95° to 100°C for 1 hour in an oven.

[0043]

The physical properties of the polyurethane foam were determined in accordance with the following methods. The results are shown in Tables 1 and 2.

[Molded Article Density]

The weight of the polyurethane foam of 100 mm × 300 mm × 10 mm was determined, and the molded article density was calculated by dividing the weight by its volume (300 cm³).

[0044]

[Hardness]

Hardness was determined by an Asker C hardness tester.

[0045]

[Tensile strength, Tear Strength and Elongation]

Each of tensile strength, tear strength and elongation is determined as prescribed in JIS K-6301.

[0046]

[Compression Set]

Compression set is determined by the method described in ASTM D 395.

[0047]

[Table 1]

Ex. No. and Comp.	Ex. No.	Ex. 1	Comp. Ex. 1	Ex. 2	Comp. Ex. 2	Ex. 3	Comp. Ex. 3	Ex. 4	Comp. Ex. 4
<u>Polyol Solution</u>									
Kind of Polyol Component		Polyol A		Polyol A		Polyol A		Polyol A	
Catalyst (TEDA) (parts)		1.2		1.1		1.2		1.1	
Crosslinking Agent (parts)		BD 10.5		EG 5		BD 10.5		EG 5	
Surfactant (SZ-1642) (parts)		1		1		1		1	
Blowing Agent (Water) (parts)		0.3		0.3		0.55		0.55	
<u>Kind of Polyisocyanate Component</u>									
		Polyisocyanate Compound A		Polyisocyanate Compound A		Polyisocyanate Compound A		Polyisocyanate Compound A	
Isocyanate Index		100		100		100		100	
Heat Treatment		con-ducted		con-ducted		con-ducted		con-ducted	
<u>Physical Properties</u>									
Density of Molded Article (g/cm ³)		0.65		0.65		0.65		0.49	
Hardness (Asker C)		70		70		60		59	
Tensile Strength (MPa)		7.8		8.5		4.1		4.4	
Tear Strength (KN/m)		30.3		30.1		17.6		17.7	
Elongation (%)		540		520		590		570	
Compression Set (%)		19.9		19.2		21.3		22.4	

[0048]

[Table 2]

Ex. No. and Comp.	Ex. No.	Ex. 5 Comp. Ex. 5	Ex. 6 Comp. Ex. 6	Ex. 7 Comp. Ex. 7	Ex. 8 Comp. Ex. 8
<u>Polyol Solution</u>					
Kind of Polyol Component		Polyol B	Polyol B	Polyol B	Polyol B
Catalyst (TEDA) (parts)		1.6	1.5	1.6	1.5
Crosslinking Agent (parts)		BD 10	EG 5	BD 10	EG 5
Surfactant (SZ-1642) (parts)		1	1	1	1
Blowing Agent (Water) (parts)		0.45	0.45	0.65	0.65
<u>Kind of Polyisocyanate Component</u>					
		Polyisocyanate Compound B	Polyisocyanate Compound B	Polyisocyanate Compound B	Polyisocyanate Compound B
Isocyanate Index		100	100	100	100
Heat Treatment		con-ducted	con-ducted	con-ducted	con-ducted
<u>Physical Properties</u>					
Density of Molded Article (g/cm ³)		0.65	0.65	0.48	0.49
Hardness (Asker C)		70	70	60	59
Tensile Strength (MPa)		7.2	7.5	3.8	4.0
Tear Strength (KN/m)		28.1	29.5	16.8	16.5
Elongation (%)		540	510	580	560
Compression Set (%)		15.2	15.6	16.8	17.5
			28.5	28.2	29.1

[0049]

It can be seen from the results shown in Tables 1 and 2 that since the heat treatment is carried out after molding, for the polyurethane foams obtained in Examples 1 to 8, the polyurethane foams are excellent in tensile strength, tear strength and compression set, as compared with those obtained in Comparative Examples 1 to 8.

Accordingly, the polyurethane foams obtained in Examples 1 to 8 are expected to be widely used for cushioning materials for shoe soles and the like.

[0050]

[Effects of the Invention]

According to the present invention, there are exhibited some excellent effects that a polyurethane foam having a satisfactory strength within the range of specific molded article densities, which can be suitably used as cushioning materials for shoe soles of sports shoes and the like, can be prepared.

[Document] Abstract

[Abstract]

[Problems]

To provide a polyurethane foam retaining high strength within a specific molded article density range and being excellent in compression set, which can be suitably used as cushioning materials such as shoe soles of sports shoes and the like.

[Solving Means]

A process for preparing a polyurethane foam, comprising reacting a polyol component having a number-average molecular weight of 1000 to 2400 with a polyisocyanate compound in the presence of a catalyst and a blowing agent, to give a molded article having a density of 0.4 to 0.8 g/cm³, and heat-treating the resulting molded article to a temperature of not less than 60°C.

[Selected Drawings] None

BACKGROUND INFORMATION OF APPLICANT

Identification Number

[000000918]

1. Date of Conversion

August 24, 1990

[Reason for Conversion]

New Registration

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